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Technical Report

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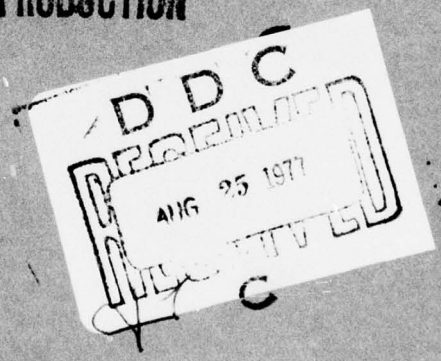
CHEMICAL CHARACTERIZATION OF NITROCELLULOSE DEGRADATION PRODUCTS



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September 1976

UNITED STATES ARMY
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An investigation of the nature of the degradation products from both steps of a chemical-bacteriological decomposition of nitrocellulose was carried out. A sensitive analytical method for nitrocellulose was perfected. A materials balance of both process steps was obtained. The chemical hydrolysis was found to give inorganic nitrites, nitrates and carbonates, and also nitrated organic oxyacids. Subsequent action by bacteria changes the product mix, but the nature of the products is essentially the same.

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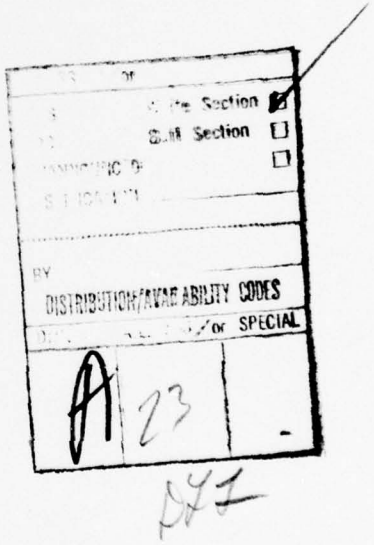
Preface

Nitrocellulose is used in propellants for various armaments. A pollution problem occurs in the clean-up of manufacturing operations and in the disposal of dated material. There was concern about the nature of the products formed in a biodegradation process used to dispose of nitrocellulose. As a consequence the U. S. Army Medical Research and Development Command requested the Pollution Abatement Group under contract #IAO 5759 to investigate the products from the biodegradation of nitrocellulose.



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Chemical Characterization of Nitrocellulose Degradation Products

Introduction: The purpose of this study was to develop techniques for the separation of individual or classes of degradation products of nitrocellulose and to characterize the type of compounds found. This information was desired in order to evaluate the polluting nature of the effluent materials so that appropriate means could be taken to minimize pollution.

Although cellulose is biodegradable, studies prior to the start of this investigation showed that direct biodegradation of nitrocellulose was not feasible. In order for some degree of biodegradation to occur, it was found that a brief alkaline hydrolysis was required. Most of the studies of nitrocellulose treatment with alkali were carried out early in the century, and the results of these studies were sketchy. In general, there is no denitration to cellulose itself. Instead, it appears that a range of highly variable decomposition products, organic and inorganic, is obtained. Thus, the study of the degradation products of the alkaline hydrolysis and subsequent biodegradation is quite intricate.

Alkaline hydrolysis of nitrocellulose: In the laboratory, the alkaline hydrolysis is carried out as a batch process. Twenty grams of nitrocellulose is suspended in a total of 400 ml of 3% sodium hydroxide, the mixture stirred and heated to 90°-95°C in a boiling water bath for 20

minutes. At this time a dark amber, clear solution is obtained. Examination of the infrared spectrum of the residue from the evaporated solution shows none of the parent nitrocellulose. The bands characteristic of nitrocellulose, at 825 and 1650 cm^{-1}, are absent. The spectrum indicates a mixture of organic and inorganic materials, and absorptions are strong in the region where carbonyl and nitro groups appear. The hydrolysis solution also gives a positive Griess test for nitro groups.

The alkaline hydrolysate was subjected to a number of preliminary studies. Portions (25 ml equivalent to 1.25 g nitrocellulose) were extracted with ether, acidified with hydrochloric acid and extracted with ether, then neutralized and again extracted with ether. Evaporation of the ether extracts yielded the following weights of residue: 2 mg from the basic solution, 57 mg from the acid extraction, and 1 mg from the neutral solution. This represents about a 5% recovery of organic substance. The acid extract was analysed in a gas chromatography and mass spectrometer. Several incompletely resolved peaks were observed in the gas chromatogram. The mass spectral analyses of a center cut of effluent from the major fraction showed the presence of two compounds. The major fragments observed were $C_3H_6NO_3+$, m/ℓ 104 and $C_3H_4NO_4+$, m/ℓ 118. This interesting finding shows that the hydrolysis of nitrocellulose with base does not remove all the nitro groups. This bears out with some of the elemental analyses of the extracts, which are discussed later.

The low weight percent recovery of organic material indicates 1) ether may not be an efficient extractor; and/or 2) a large loss of volatiles; e.g., low boiling point organics and inorganic gases such as ammonia, nitric oxides, and carbon dioxide. Steam distillations of the hydrolysate solution, neutralized and acidified, were not successful for the isolation of any compounds.

Material balance studies of the basic hydrolysate: The material balance, although not being specific for individual compounds, will establish total carbon, organic carbon, nitrogen, nitrates, and nitrites, in order to establish criteria for the evaluation of the nitrocellulose waste waters.

Several determinations were made of weight losses by evaporation and ignition under different conditions. When the base hydrolysate solutions of nitrocellulose are evaporated on a steam bath and then desiccated, there remains a light tan powderable solid. This material is very hygroscopic. On acidification with dilute hydrochloric acid, there is much effervescence. The dry residue, before acidification, shows a 3.6% loss in total weight, based on nitrocellulose and sodium hydroxide; after acidification, reevaporation on a steam bath, and desiccation. The weight loss amounts to 21%.

Infrared measurements of the residue from the hydrolysis show an absence of the 825 and 1650 cm^{-1} bands characteristic of nitrocellulose. The spectrum indicates a mixture of organic and inorganic material, and the presence of nitro groups, the residue remaining after

evaporation of the acidified solution shows some slight changes in the infrared measurements. The Griess spot test for nitrate is positive for these residues.

Ignition loss determinations, according to the German Standard Method (DEV) were carried out on the basic hydrolysate. This procedure gives an indication as to the amount of organic materials. The ignition is carried out at a temperature of 600°-650°C. These conditions will also cause inorganic nitrates and carbonates to lose nitroxide and carbonic gases. A 66% weight loss was found. When the acidified hydrolysate was ignited in the same manner, there was a 31% loss in weight.

The gases which arise on acidification of the base hydrolysate residue were investigated. Nitric oxides were detected easily by the appearance of brown fumes and their characteristic odor. The gases were collected in an infrared cell and measured. Absorption bands characteristic of carbon dioxide and nitric oxides were observed.

Isolation procedures for organic materials: Two principal procedures were pursued for the separation of the organic from inorganic substances. In the first procedure we utilized column chromatography with Amberlite resins. These resins are a group of polymeric absorbents from Rohm and Haas Co. Experiments showed that XAD-7, a polyacrylic ester of intermediate polarity, gave the cleanest separation of organic material. The hydrolysate solutions with pH 12.5 were adjusted to pH 2.5 with

dilute hydrochloric acid. This solution was then washed through a column of XAD-7 resin with several volumes of water. The inorganic material is washed through in the procedure, and the organic material adsorbed onto the resin. Elution of the column with methanol removed the organic substances. Twenty-ml samples yielded an average 35 mg of organic material, obtained after removal of solvent and desiccation, as a tan solid which was hygroscopic. Infrared measurements of these methanol residues showed bands characteristic of a mixture of hydroxy-carboxylic acids. For example, comparison of the spectra of glycolic acid and the residue spectra were very similar. Elemental analysis, however, shows also the presence of nitrogen (C, 40.80; H, 4.66; N, 3.79%). Therefore nitro groups are probably present. Preliminary attempts to separate the mixture by high pressure liquid chromatography on an ODS-H_2O column have not been successful.

The second technique for the separation of organics involves extraction procedures with organic solvents. Benzene and methylene chloride were very poor in removing anything from the acidified aqueous solutions. Ether yielded about 1% of organic material (based on the original weight of nitrocellulose). We were able to extract the most material with acetone. Normally, due to the complete solubility of acetone with water, acetone is not considered suitable as an extraction solvent. However, by saturation of the aqueous solution with sodium chloride, the solubility of acetone is greatly reduced, and immiscible layers are formed. After the acetone extract is evaporated to dryness,

the residue still contains some salt. This is removed by washing the dry residue with acetone, evaporation to dryness, and a repetition of this step. About 15 to 20 percent of organic material was obtained. Comparison of the infrared spectra of the ether and acetone extracts showed slight differences. Elemental analyses showed nitrogen present (C, 36.65; H, 4.27; N, 8.37%).

The acetone extract was distilled in a short-path apparatus, in vacuo. At a pot temperature of 90°C at 0.25 mm pressure, white crystals deposited on the condenser walls. Surprisingly, the infrared spectrum of this substance was not very different from the starting material. The distillation yielded only a very small fraction, and there was much charred residue in the pot. Treatment of some of the distillate with ethereal diazomethane yielded a liquid whose infrared spectra indicated possible conversion of hydroxyl groups to methoxyl.

Biodegradation effluents: Investigation of the solutions from the biodegradation reaction involved similar procedures to those with the base hydrolysate. In the biodegradation process the final solutions are much more dilute (there is over a tenfold nonquantitative dilution), and since the technique is essentially a flow-through procedure, rather than a batch process, the material balance on the basis of original nitrocellulose is not meaningful.

Samples of the solutions were freeze-dried at original pH 10, and after acidification to pH 5.7. There was a 37% loss in weight after

acidification. The infrared spectra showed minor changes. The gases evolving from the acidification again proved to be carbon dioxide and nitric oxides.

Ignition loss determinations showed a 32% decrease in weight (when compared to amount of residue obtained from evaporation of an equal volume of biodegradation solution), and a 29% decrease in weight from the residue of acidified solution. The smaller ignition losses found for the biodegraded solutions in comparison to the basic hydrolysates may signify that the biodegradation has further broken down some of the larger molecules to more volatile compounds, which are then lost to the atmosphere.

A 250-ml sample, adjusted to pH 2.5 yielded in acetone extractions (as previously described) on the average 15 mg of material. The infrared spectra and elemental analyses of the extraction residue indicated that this residue is similar to that obtained from the base hydrolysate.

Infrared analyses of nitrocellulose: For the general analyses of nitrocellulose, infrared spectroscopic techniques have been investigated and shown to be the most useful and convenient for both qualitative and quantitative measurements. A good indication of the presence of nitrocellulose involves examination of the infrared spectrum, obtained from pressed potassium bromide dispersions, at 825, 1275, and 1650 cm^{-1}. These are strong bands related to the nitrate ester groups. Quantitative measurements are possible by preparing calibration curves for acetone

solutions of nitrocellulose, using the 825 cm^{-1} absorption band. This wavelength is not subject to interference from other cellulosic materials. When inorganic nitrites interfere, the 1650 cm^{-1} band is utilized with tetrahydrofuran as a solvent. This technique allows concentration measurements in the 1-5 ppm range.

Review and future aspects: Many of the experiments were of an exploratory nature in order to determine the most useful procedures. It appears that there is probably less residual material remaining from the biodegradation, although the residue may not be much different from that obtained in the initial basic hydrolyses. The inorganic material remaining after the degradation process is probably a mixture mostly comprised of sodium carbonate, nitrate, and nitrite. A quantitative estimation of these inorganics in the process liquors will allow us to plan for appropriate conversion to useful form or disposal.

Treatment of the crude degradation liquors with Amberlite resins may be a very useful large scale technique for separation of the organic from inorganic material. These resins are attractive since they can be reused with simple regeneration methods.

Conclusion: In general, it appears that the residual organic materials from the basic hydrolysis of nitrocellulose and its subsequent biodegradation are similar. The organic residue is apparently a mixture of very many compounds, the bulk of which are nitrated hydroxy acids.

Future work should be directed to the isolation and identification of these compounds. Also, the more volatile organic materials should be trapped and investigated.

Appendix - Infrared Spectra

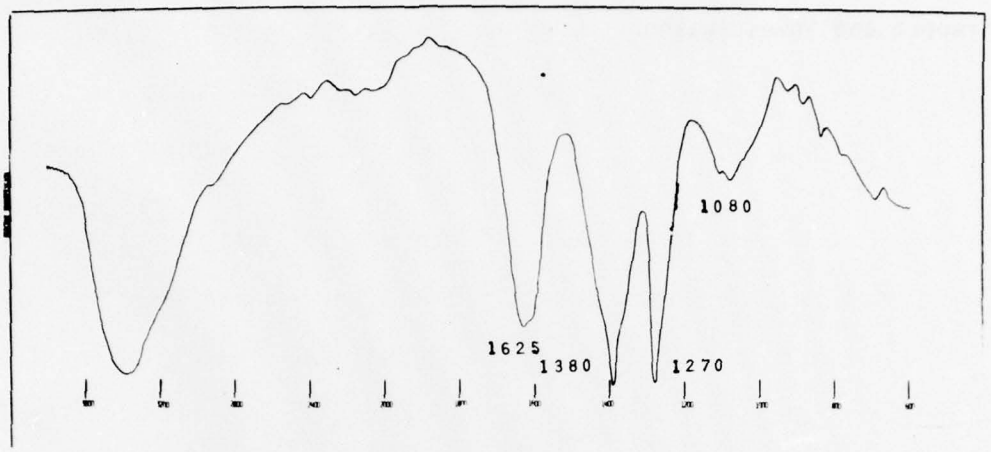


Fig. 1. Residue from the basic hydrolysate of nitrocellulose.

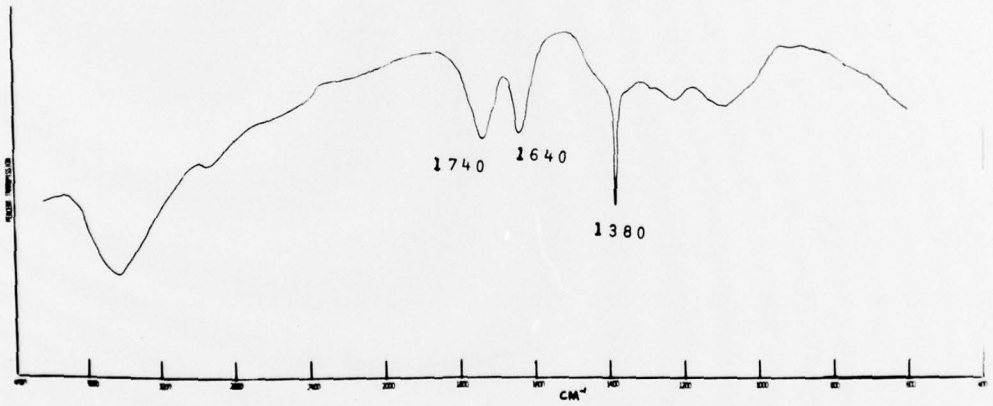


Fig. 2. Residue from the acidified basic hydrolysate of nitrocellulose.

Comments (Fig. 1 & 2): Only very general comments apply to these spectra since they represent a mixture of organic and inorganic compounds. After acidification (Fig. 2), a new absorption band is seen at 1740 cm^{-1}, most likely from carboxylic acid function. This group, as the sodium salt, is seen in Fig. 1, at 1625 cm^{-1}. The inorganic sodium nitrate band at 1380 cm^{-1} is found in both spectra. Inorganic nitrites and carbonates which degasify on acidification contribute to the 1270 and 1380 cm^{-1} bands.

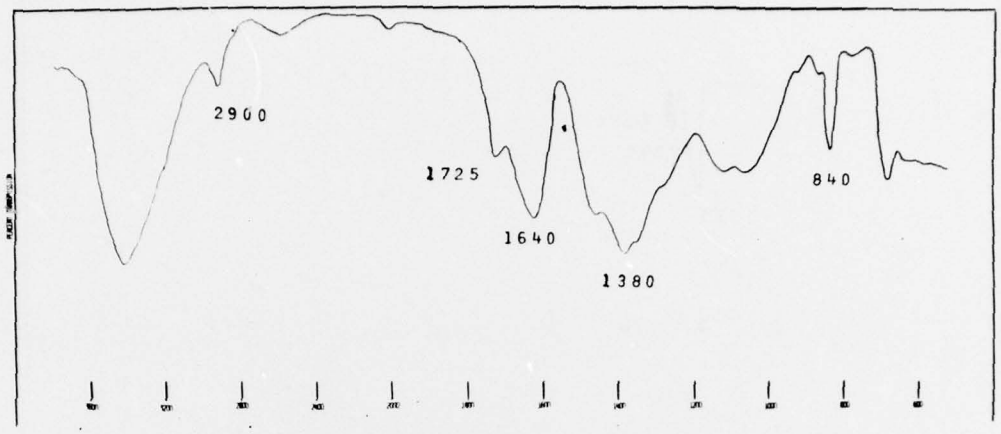


Fig. 3. Residue from the biodegraded effluent of nitrocellulose

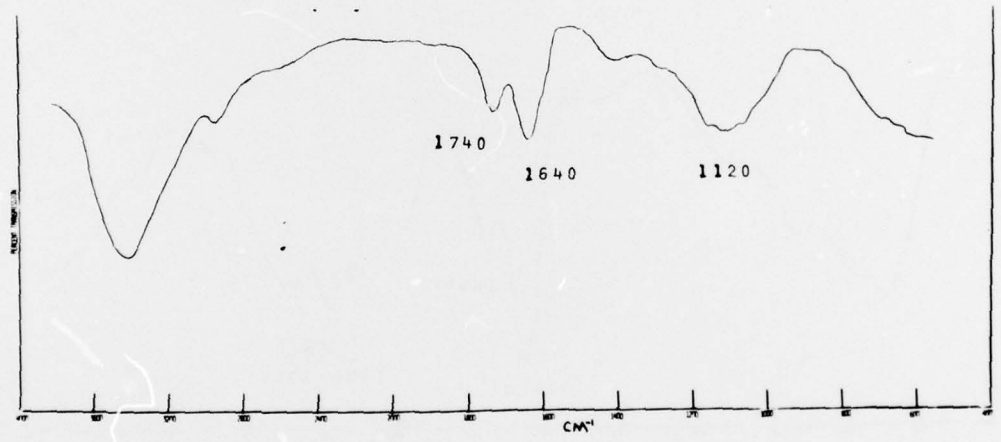


Fig. 4. Residue after acidification of biodegraded effluent of nitrocellulose.

Comments (Figs. 3 & 4): As in Figs. 1 & 2, we have here again a mixture of organic and inorganic materials. The bands at 1640 and 1740 cm^{-1} are likely due to carboxylic acid groups. Nitro groups are also contributing to the 1640 cm^{-1} band. Fig. 4, although not a well-defined spectrum, is similar to that of Fig. 2, except for the inorganic nitrate band at 1380 cm^{-1}.

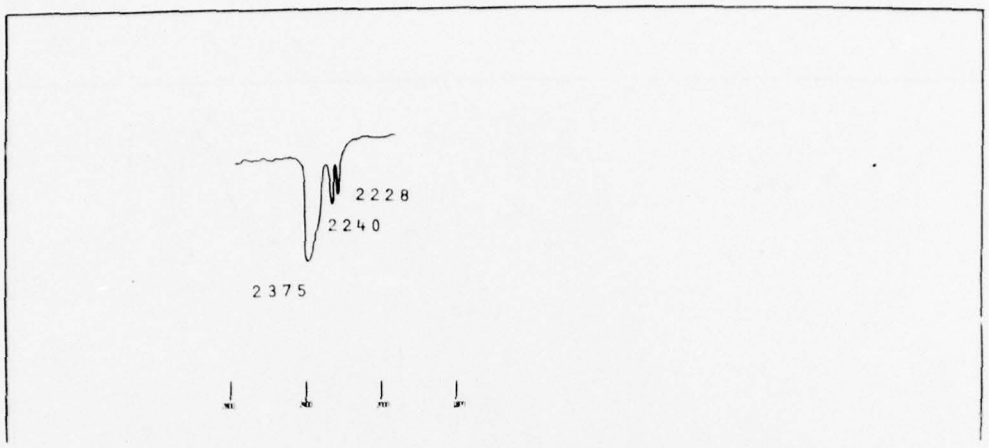


Fig. 5. Gases formed by acidification of either the basic hydrolysate or biodegraded effluent.

Comments (Fig. 5): The 2375 cm^{-1} band is due to carbon dioxide, and the doublet, 2228-2240 cm^{-1} arises from nitrogen oxide.

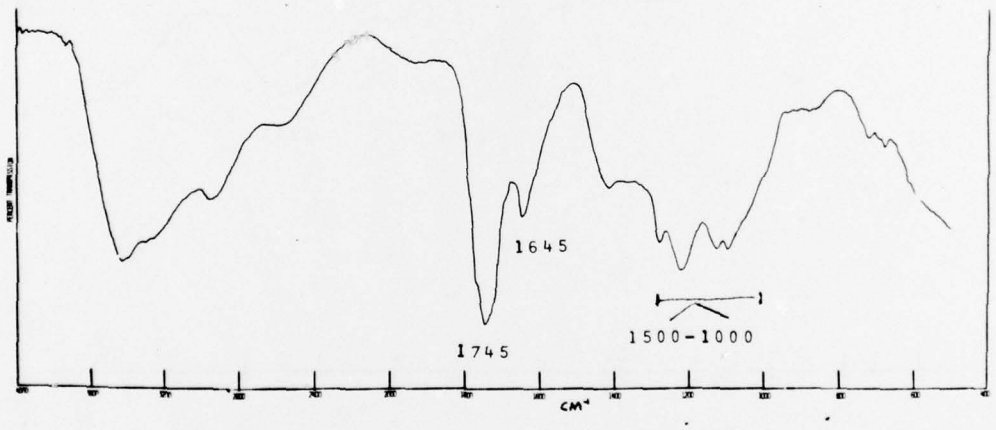


Fig. 6. Acetone extract of acidified solution of the base hydrolysate of nitrocellulose.

Comments (Fig. 6): In this spectrum the carbonyl function is much more prominent at 1745 cm^{-1}. Nitro group bands may be contributing to at 1645 and 1000-1500 cm^{-1}. The spectrum has many similarities to hydroxy carboxylic acids such as that of glycolic acid (Fig. 11).

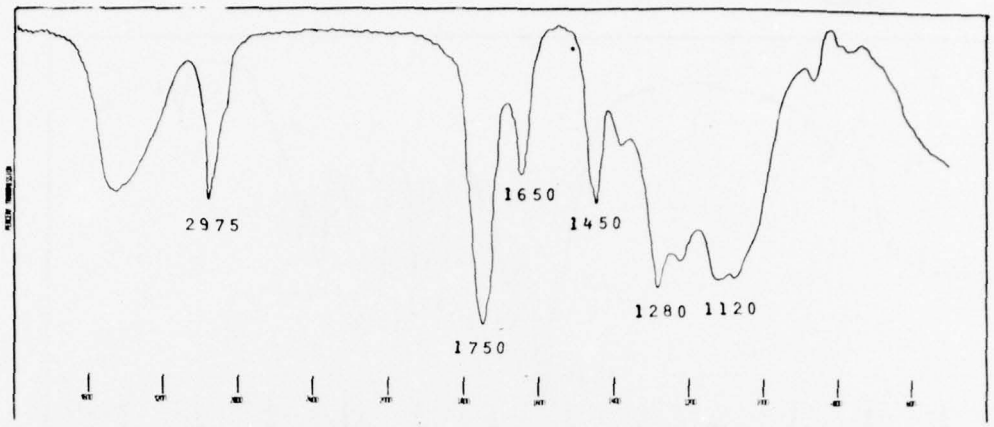
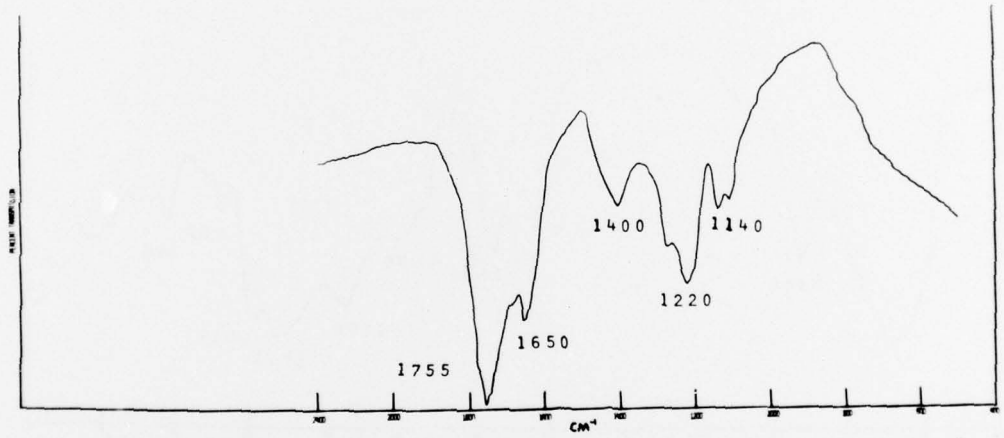


Fig. 7. Oil from treatment of acetone extract shown in Fig. 6, with ethereal diazomethane.

Comments (Fig. 7): New prominent bands are seen at 1450 cm^{-1}, most likely due to the CH bending mode of OCH_3 group formed from hydroxyl group, and at 2975 cm^{-1}, due to CH stretching modes.



Comments (Fig. 8): Very similar to the starting material of Fig. 6.

Fig. 8. White crystalline residue distilled from residue of acetone extract of the base hydrolysate of nitrocellulose (Fig. 6).

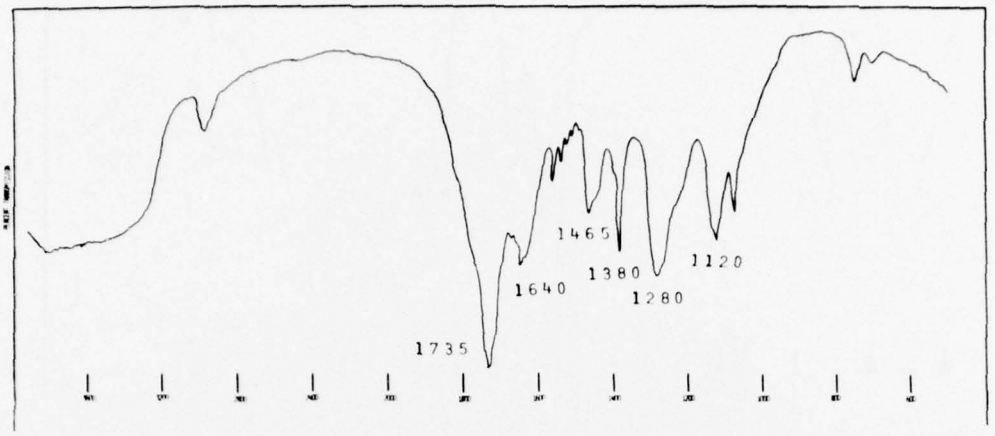


Fig. 9. Oil from the treatment of the distillate (Fig. 8) with ethereal diazomethane.

Comments (Fig. 9): Similar to Fig. 7. The absorptions are sharper than in Fig. 7 and it appears that the reaction with diazomethane is more complete.

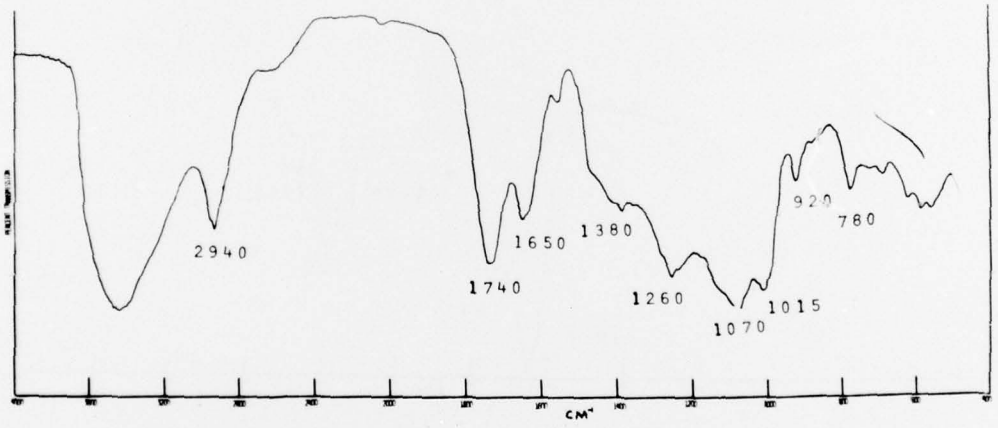


Fig. 10. Organic elutant through XAD-7 resin from the acidified solution of the basic hydrolysate of nitrocellulose.

Comments (Fig. 10): Spectrum appears to be due to a mixture of materials and is similar to the spectrum from the acetone extract (Fig. 6). Also has many characteristics of hydroxy carboxylic acids.

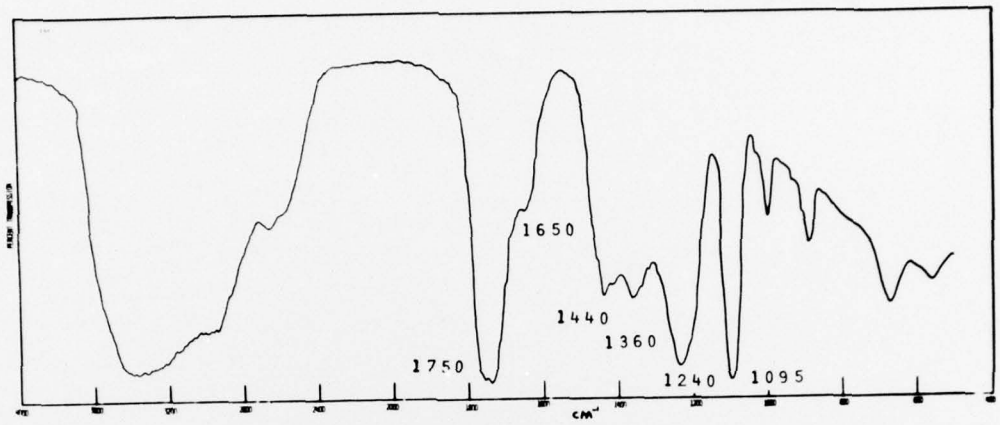


Fig. 11. Glycolic acid.

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